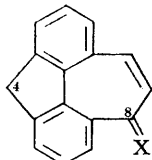
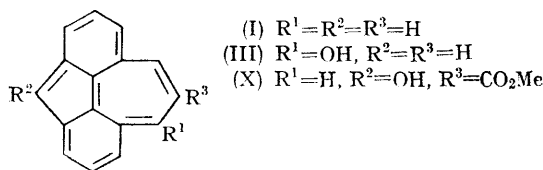


Synthetic Approaches to the Cyclohepta[*def*]fluorene System

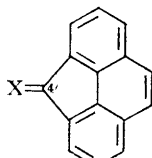
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It has recently been predicted by Heilbronner¹ that the hydrocarbon, cyclohepta[*def*]fluorene (I) would either be a ground-state triplet or have a low-lying triplet state. We now report the synthesis of 8-oxo-4*H*-cyclohepta[*def*]fluorene (II) which is potentially tautomeric with 8-hydroxy-cyclohepta[*def*]fluorene (III).



(VII) $X=H_2$



(VIII) $X=O$

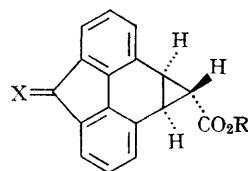
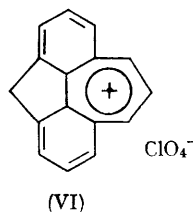
The reaction of 4*H*-cyclohepta[*def*]phenanthrene² (IV) with ethyl diazoacetate at 145—150° readily yielded the *exo*-norcaradiene derivative (V), m.p. 141—142°, the stereochemistry of which is readily assigned by comparison of the nuclear magnetic resonance (n.m.r.) spectrum of (V) with the spectra of the *endo*- and *exo*-phenanthrene³ and pyrene^{†4} adducts with ethoxycarbonylcarbene which have structures analogous to (V). The adduct (V) was hydrolysed to the corresponding acid which reacted with lead tetra-acetate in benzene solution to give the tropone derivative (II) (26% yield), m.p. 168°. The n.m.r. spectrum of (II) in deuteriochloroform was consistent with the assigned structure [τ 1.67, quartet, 1H, H-7; τ 2.2—2.8, multiplet, 6H, H-10 and remaining aromatic protons; τ 3.21, doublet ($J = 13$ c./sec.), 1H, H-9; τ 6.13, singlet, 2H, H-4] as were the infrared and ultraviolet spectra; there was no evidence for any equilibrium with the tautomer (III). Reduction of (II) with lithium aluminium hydride and reaction of the total crude product with ethereal perchloric acid precipitated a red crystalline salt formulated as (VI) on the basis of

† The *exo*-adduct of methoxycarbonylcarbene and pyrene has been reported (ref. 4); our investigation of the reaction with ethoxycarbonylcarbene shows that both the *exo*- and the *endo*-adducts are formed in this case.

its ultraviolet spectrum [λ_{\max} (ϵ) in 20N-H₂SO₄, 234 (11,500), 246 (12,300), 281 (29,700), 300 (19,200), 323 (15,500), 481 m μ (6600)] which strongly resembled that of dibenzo[*a,c*]tropylium sulphate.⁵ The tropylium salt (VI) failed to yield cyclohepta[*def*]fluorene on reaction with ethereal triethylamine; the product had a molecular weight (204, mass spectrum) corresponding to that of 4,8-dihydrocyclohepta[*def*]fluorene (VII) but the quantity obtained was insufficient for complete characterisation. Exposure of this product to air resulted in the formation of the tropone (II).

A parallel approach to the cycloheptafluorene system utilised the reaction of 4-oxo-4*H*-cyclopenta[*def*]phenanthrene² (VIII) with methyl diazoacetate. The product, m.p. 176°, had an n.m.r. spectrum consistent with the *exo*-structure (IX) and although (IX) is potentially tautomeric with the cycloheptafluorene derivative (X) there was no evidence for the presence of (X) in solution.

The results obtained in this investigation suggest that the cyclohepta[*def*]fluorene system does not have the stability associated with a polycyclic aromatic system. This conclusion is in accord with the theoretical treatment which predicts either a destabilised singlet ground-state or a triplet ground-state.



(V) X=H₂, R=Et
(IX) X=O, R=Me

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